

ms B1

PROCESS FOR THE MANUFACTURE OF DISPERSIBLE ALUMINO-SILICATES

The present invention relates to a process for the manufacture of high-purity alumino-silicates which are dispersible in aqueous or aqueous-acidic media by hydrolysis of aluminium compounds and organosilicon compounds.

10 There exists a large number and wide variety of natural alumino-silicates, including many compounds having defined crystalline structures, such as muscovite, nepheline, and chabasite. When exchanging part of the silicon atoms in the reticulation of silicates for aluminium atoms, without destroying the reticulation, zeolites are obtained.

15 Besides natural alumino-silicates, there are many synthetic products of this kind. Such products may be those defined by crystal chemistry or may be physical mixtures of aluminium hydroxide and silicic acids with different quantities of water. Besides physical mixtures, alumino-silicate defined by
20 crystal chemistry may be present as well.

A customary process for preparing such alumino-silicates is the conversion of clays, such as kaolin, using silicic acid and sodium hydroxide. Another synthesis route is the cogelation of aluminium hydroxide sols with silicic acid sols
25 followed by precipitation [cf. GB 2166971-C]. Precipitation of an aluminium salt in a silicic acid sol is known as well [cf. CA 848966-A].

The aforesaid processes have the disadvantage that the desired sols or emulsions only exist at the instant they are prepared, while the powder obtained
30 by subsequent drying can only incompletely be dispersed or requires solvent mixtures to achieve dispersion. Another disadvantage is that the sols or emulsions prepared in this way contain large quantities of alkali metals or alkaline earth metals used for stabilising the silicic acid. Subsequent purification, e. g. by ion exchange, is incomplete and results in typical concentrations of alkali
35 metals or alkaline earth metals of 0.1 % (equal to 1,000 ppm) after purification [cf. US 3,933,621].

10054330-012302

Heterogeneous catalysis requires high-purity catalyst supports containing less than 100 ppm of alkali metals and/or alkaline earth metals, particularly less than 50 ppm of sodium oxide. The preparation of such high-purity aluminosilicates using ion exchanged ortho-silicic acid is described in German patent DE 38 39 580 - C1. The resultant aluminosilicates have the desired high purities, but they cannot be dispersed.

Aluminosilicates are physically/chemically not comparable with aluminium hydroxides. For instance, their surfaces have higher acidities due to the stronger Lewis acid character of silicic acid. This property is utilized for a large number of catalytic processes, such as desulfurizing, denitrification, oxidation, hydrocracking, and mild hydrocracking.

Modern catalysts often consist of many different support materials [for instance, cf. GB 2166971-C]. It is essential that the catalyst support materials be homogeneously mixed to ensure uniform compositions. Therefore, dispersible aluminosilicates offer several advantages, e. g. when used for coating substrates. This method can be used in the field of catalysis and materials coating. The explanations given hereinabove show that there is a need for dispersible high-purity aluminosilicates.

It was the object of this invention to develop a synthesis for preparing dispersible aluminosilicates which offers the following advantages:

- Even after drying and conversion into powder, the aluminosilicates prepared according to the present invention shall be dispersible in aqueous solutions without addition of or treatment with organic solvents.
- The aluminosilicates prepared according to the present invention shall have high purities.
- The starting materials used for preparing the aforesaid compounds shall be readily available.

- The Si/Al ratio of the product shall be adjustable by varying the educt ratio and without using one of the components in excess.
- The price of the starting materials shall allow an economic process.
- The manufacturing process shall be feasible both as a continuous and discontinuous process.

It was surprisingly found that the process described hereinbelow provides alumino-silicates which solve the problems the present invention was based on.

The instant invention relates to a process for the continuous or discontinuous manufacture of high-purity alumino-silicates which can be dispersed in aqueous and/or aqueous-acidic media. The desired properties are obtained by the following process:

Process for the manufacture of alumino-silicates which are dispersible in aqueous and/or aqueous-acidic media wherein

- (A) one or more hydrolyzable aluminium compound(s) and
- (B) one or more hydrolyzable organosilicon compound(s)

is (are) hydrolyzed. The components are hydrolyzed jointly. Alternatively, they can be hydrolyzed consecutively or separately. In the latter case, the (partial) reaction products will be combined after the (partial) hydrolysis.

Hydrolyzable compounds within the meaning of the instant invention are all the aluminium compounds or organosilicon compounds forming M-OH and/or M-O-M structures when reacted with water, e. g. organosilicon compounds, such as silicones, alkyl silanes, alkyl alkoxysilanes, alkyl halogen silanes, alkoxyhydroxysilanes, or alkyl hydroxysilanes, or aluminium compounds, such as aluminium alcoholates, aluminium hydroxy-alcoholates, aluminium oxyalcoholates, aluminium acetyl acetates, aluminium alkyl chlorides, or aluminium carboxylates. The hydrolysis may be carried out at 20 to 98 °C, preferably 50 to 98 °C, most preferably 85 to 98 °C.

Preferably, compounds of the type $M(O-R-A-R')_{z-n} (O-R'')_n$ are employed, wherein independent of each other and, optionally, different for each residue

M is aluminium or silicon,

R'' is a branched or an unbranched, a cyclic or an acyclic, or an aromatic hydrocarbon residue having 1 to 30, particularly 2 to 12 carbon atoms,

R' is a branched or an unbranched, a cyclic or an acyclic, or an aromatic hydrocarbon residue having 1 to 10 carbon atoms, particularly an alkyl residue having 4 to 8 carbon atoms,

R is a bivalent and branched or unbranched, cyclic or acyclic, or aromatic C₁ to C₁₀ hydrocarbon residue, particularly an alkyl residue having 1 to 5 carbon atoms, most preferably 1 to 3 carbon atoms, the latter one most preferably being unbranched and acyclic,

A represents a heteroatom of main group 6 (oxygen group) or main group 5 (nitrogen group) of the periodic system, preferably oxygen or nitrogen, wherein, if A represents an element of main group 5, A bears hydrogen or a C₁ to C₁₀ alkyl residue or a C₆ to C₁₀ aryl -/alkyl aryl residue as additional substituent(s) for the saturation of its valences, and

n is an index for the numbers 0, 1, 2, or 3 if M is aluminium, or is an index for the numbers 0, 1, 2, 3, or 4 if M is silicon, and

z is an index for the number 3 if M is aluminium, or is an index for the number 4 if M is silicon.

Preferably, n is equal to 0 or equal to 3 if M is aluminium. If M is silicon, n is preferably equal to 4. If n is equal to 0 and A is oxygen, metal trisbutylene glycolates are preferred. It is preferred that M be aluminium.

In case n is equal to 3, the aluminium compounds are aluminium trisalcoholates which, with increasing preference, have C₂ to C₁₂, C₄ to C₈, or C₆ to C₈ hydrocarbon residues, the residues being saturated or unsaturated, cyclic or acyclic, branched or unbranched, or aromatic, preferably saturated. Saturated, linear C₆ to C₈ hydrocarbon residues are particularly preferred. For example, hydrolyzable aluminium alcoholates may be prepared according to the process disclosed in EP 0 111 115 - A1.

In case n is equal to 4, the hydrolyzable organosilicon compounds are silicon alcoholates. Preferred silicon alcoholates have C₁ - C₈ hydrocarbon residues, the residues being saturated or unsaturated, cyclic or acyclic, branched or unbranched, or aromatic. Saturated C₂ to C₄ hydrocarbon residues are particularly preferred.

Furthermore, the process according to the instant invention is superior by the fact that, apart from the educts or products, the reaction can be carried out without any organic solvents and in an essentially aqueous or alcoholic/aqueous environment.

According to an embodiment of the present process, the hydrolyzable organosilicon compounds are prehydrolyzed or partially hydrolyzed prior to addition of the hydrolyzable or hydrolyzed aluminium compound with 0.5 to 3 moles of water, preferably 1 to 2 moles, per mole of silicon, i.e. less than the stoichiometric amount. Said partial hydrolysis is preferred, whenever the hydrolyzable aluminium compound is not of the type $\text{Al}(\text{O}-\text{R}-\text{A}-\text{R}')_{3-n}(\text{O}-\text{R}'')_n$.

Prior to use, the hydrolyzable metal compounds may be purified by distillation, filtration, ion exchange and/or centrifugation.

In addition, dispersibility improves by several percent when the combined reaction products of the silicon and aluminium compounds are subjected during or after the hydrolysis to joint hydrothermal treatment in an aqueous environment at temperatures of 40 to 220 °C for a period of greater than 0.5 hour. In another embodiment of this process the hydrothermal ageing is performed during a period of 0.5 to 24 hours. Preferably, the treatment is performed at temperatures of 80 to 130 °C for a period of 1 to 20 hours, most preferably 5 to 20 hours.

Optionally, an acid may be present during the hydrothermal treatment. It is preferred that this acid be a monovalent organic C₁ to C₆ acid or a monovalent inorganic acid (a monovalent mineral acid), such as HCl or HNO₃. The acid may also be added after the hydrolysis, but it should be added before drying and should be present during the hydrothermal treatment.

It can be used in quantities of 0.1 to 2.0 grams, preferably 0.2 to 0.8 gram, referring to 1 gram of solid material.

Within the meaning of the present invention, monovalent organic C_1 to C_6 acids are organic compounds which have at least 1 to 6 carbon atoms and show an acid reaction in the presence of water, i.e. react as proton donors, and which can set free only one proton, referring to the acid molecule. This definition includes for instance acid chlorides, sulfonic acids, and other organic compounds forming $-COOH$ or $-COO^-$ groups in water.

The educts may be used in quantities of from 99.5 wt.% : 0.5 wt.% to 50 wt.% : 50 wt.%, preferably from 98 wt.% : 2 wt.% to 50 wt.% : 50 wt.%, each referring to the ratio of Al_2O_3 : SiO_2 . Bases, such as ammonia solution, may be added after the hydrolysis in order to achieve better separation of the organic phase. Furthermore, the reaction product of this invention can be calcined at temperatures of 550 °C to 1,500 °C for a period of 0.5 hour to 24 hours.

The dispersible alumino-silicates are useful as catalysts, catalyst supports for catalytic processes, for the manufacture of catalysts, as starting materials for ceramics, as coating materials, and as binder components and rheological modifiers in aqueous systems.

The term 'dispersible alumino-silicates' as used in the present invention means dry and, most expediently, powdery alumino-silicates which can be dispersed in aqueous media in quantities of at least greater than 90 wt.%, preferably greater than 95 wt.%, i.e. greater than 90 wt.%, preferably greater than 95 wt.% of said products will remain dispersed after dispersion. In the experimental part described hereinbelow a method for quantifying the dispersibility is described. The resultant aqueous products can be dried using known methods, such as spray drying or by means of a rotary drier. The process for manufacturing alumino-silicates according to this invention can be carried out continuously or discontinuously.

The alumino-silicates of this invention can be dispersed using water-diluted acids, such as inorganic acids, e. g. hydrochloric acid, nitric acid, or C₁ to C₆ organic acids, monovalent acids being preferred. The acids used for dispersion can be employed in concentrations of 0.1 to 40 wt.%, referring to the straight acid. Preferably, lower concentrations are used, i. e. from 0.1 to 5 wt.%. In some cases it is also possible to use only water for dispersion.

The compounds manufactured according to this invention can be calcined in a furnace at temperatures of 550 °C to 1,500 °C for a period of 3 to 24 hours. The metal oxide manufactured in this way has the requisite high purity.

Table 1, following, shows several alumino-silicates manufactured according to the present invention and their dispersibilities D.

Table 1

Compound	Al ₂ O ₃ : SiO ₂ [wt. %]	HNO ₃ [wt. %]	Ageing [h / °C]	Dispersibility D [%]
1	72.3 : 27.7	30.0	-	96
2	61.5 : 38.5	25.0	-	96
3	72.3 : 27.7	2.0	16 h / 95 °C	97
4	51.6 : 48.4	30.0	-	95
5	95.0 : 5.0	0.8	16 h / 95 °C	97
6	74.1 : 25.9	30	-	98
A	95.1 : 4.9	30	-	nondispersible
B	50.4 : 49.6	30	-	nondispersible
C	68.8 : 31.2	30	5 h / 95 °C	nondispersible

Legend: Compounds A and B are conventionally produced alumino-silicates.

C is an alumino-silicate prepared from silicic acid and aluminium alcoholates, including hydrothermal treatment, but without addition of an acid.

A through C are reference substances; 10 weight percent of each solid alumino-silicate were dispersed.

• acid for dispersion

Table 2, following, shows the physical data of the alumino-silicates according to this invention in comparison with two standard alumino-silicates (A and B). The reference alumino-silicates A and B were prepared by mixing an alumina sol with silicic acid.

Table 2

Compound	Al ₂ O ₃ : SiO ₂ [wt.%]	Surface [m ² /g]	Pore Volume [ml/g]
1	72.3 : 27.7	426	0.41
2	61.5 : 38.5	406	0.35
3	72.3 : 27.7	315	0.22
4	51.6 : 48.4	303	0.31
5	95.0 : 5.0	527	0.73
6	74.1 : 25.9	500	0.62
A	95.1 : 4.9	314	0.54
B	50.4 : 49.6	452	0.60

The dispersible alumino-silicates manufactured according to this invention have high purities. In particular, the content of alkali metals and alkaline earth metals which have particularly adverse effects when using the aforesaid products for catalysis is very low. The results of the trace elements analysis by ICP spectroscopy are listed in Table 3. The purities listed in Table 3 can be further increased by using bidistilled water and containers made of inert materials.

Table 3

Compound	Na ₂ O [ppm]	Li ₂ O [ppm]	MgO [ppm]	CaO [ppm]	TiO ₂ [ppm]	Fe ₂ O ₃ [ppm]
1	13	< 5	< 10	< 10	< 50	12
2	< 10	< 5	< 10	< 10	< 50	48
4	16	< 5	< 10	< 10	< 50	63
5	< 10	< 5	< 10	< 10	< 50	28
6	12	< 5	< 10	< 10	< 50	35

Legend: The concentration of other elements, such as Pb, Zn, Ni, Cr, Cu, Mn, Mo, and Ga, is less than 50 ppm in total.

10 Examples (General)

The compounds prepared according to this invention were analysed for trace impurities by inductively coupled plasma (ICP) spectroscopy. The surfaces were determined by the BET method, while the pore volumes were additionally
 15 determined by mercury porosimetry (Autopore II 9220 porosimeter, Mikromeritics) and nitrogen porosimetry (Flow Prep 060, Gemini 2360, 2375, Mikromeritics). The compounds of this invention were calcined in a muffle furnace at temperatures of between 550 °C and 1,500 °C. Deionised water was used for the hydrolysis.

20 The dispersibility D was determined by the following method. A certain amount of the dry, solid material was placed into a beaker and mixed with dilute acid, e. g. nitric acid, while stirring. Stirring was continued for 10 minutes (stirrer speed 800 – 850 rpm). The suspension thus obtained was
 25 quantitatively transferred to the glass tube of a centrifuge. Subsequent to centrifugation for 20 minutes at 2,400 rpm⁻¹, the supernatant was decanted, and the residue in the glass tube was dried for at least 0.5 hour at 573 K (300 °C). The glass tube then was weighed including the residue, and thereafter without residue. The difference obtained is the weight of nondispersed
 30 solid.

Nondispersed quantity, % = $\frac{\text{gram of residue} \times 100}{\text{initial weight of alumina, in grams}}$

Dispersed quantity D, % = 100 - percentage of nondispersed quantity

Example 1 (Compound 1)

Into a 1,000-ml three-neck flask, there were placed 136.4 grams of silicon tetraethanolate (14.25 wt.%). The contents was heated to 90 °C. Addition of 11.8 grams of 1 % nitric acid resulted in moderate precipitation. After stirring for 1 hour, 400 grams of aluminium trishexanolate (6.3 wt.%) were added.

Then, this mixture was added in three portions to 686 grams of water heated to 90 °C in order to perform the hydrolysis. Hydrolysis took 1 hour. During this period, after 40 minutes, 8.4 grams of 25 % ammonia solution were added to facilitate phase separation. The supernatant alcohol was decanted and the remaining aqueous phase was liberated from alcohol residue by steam distillation, followed by spray drying.

Example 2 (Compound 2)

Into a 1,000-ml three-neck flask, there were placed 212 grams of silicon tetraethanolate (14.25 wt.%). The contents was heated to 90 °C. Addition of 18.4 g of 1 % nitric acid resulted in moderate precipitation. After stirring for 1 hour, 400 grams of aluminium trishexanolate (6 wt.%) were added. Then, this mixture was added in three portions to 778 grams of water heated to 90 °C in order to perform the hydrolysis. Hydrolysis took 1 hour. During this period, after 40 minutes, 9.6 grams of 25 % ammonia solution were added to facilitate phase separation. The supernatant alcohol was decanted and the remaining aqueous phase was liberated from alcohol residue by steam distillation, followed by spray drying.

Example 3 (Compound 3)

5 Into a 1,000-ml three-neck flask, there were placed 179 grams of silicon tetra-
ethanolate (14.25 wt.%). The contents was heated to 90 °C. Addition of 15.5 g
of 1 % nitric acid resulted in moderate precipitation. After stirring for 1 hour,
500 grams of aluminium trishexanolate (6.3 wt.%) were added. Then, this
mixture was added in three portions to 883 grams of water heated to 90 °C in
10 order to perform the hydrolysis. Hydrolysis took 1 hour. After addition of 8.5
grams of HNO₃ (65 wt.%), ageing was performed at 95 °C for 16 hours. The
supernatant alcohol was decanted and the remaining aqueous phase was lib-
erated from alcohol residue by steam distillation, followed by spray drying.

15 Example 4 (Compound 4)

20 Into a 1,000-ml three-neck flask, there were placed 318 grams of silicon tetra-
ethanolate (14.25 wt.%). The contents was heated to 90 °C. Addition of 27.5 g
of 1 % nitric acid resulted in moderate precipitation. After stirring for 1 hour,
400 grams of aluminium trishexanolate (6.3 wt.%) were added. Then, this
mixture was added in three portions to 870 grams of water heated to 90 °C in
order to perform the hydrolysis. Hydrolysis took 1 hour. During this period,
after 40 minutes, 11 grams of 25 % ammonia solution were added to facilitate
phase separation. The supernatant alcohol was decanted and the remaining
25 aqueous phase was liberated from alcohol residue by steam distillation, fol-
lowed by spray drying.

Example 5 (Compound 5)

30 In a 1,000-ml three-neck flask, there were mixed 550 grams of aluminium
trisbutylene glycolate (Al content 5.6 wt.%) and 21.4 grams of silicon tetra-
ethanolate (14.25 wt.%). This mixture was added in three portions to 735 g of
water and 6.2 g of HNO₃ (65 wt.%) heated to 75 °C in order to perform the hy-
drolysis. Hydrolysis took 1 hour. After phase separation, the supernatant or-
35 ganic phase was decanted. The aqueous phase was heated to 95 °C and main-
tained at this temperature for 16 hours. The alcohol in the aqueous phase
was eliminated by steam distillation, followed by spray drying.

Example 6 (Compound 6)

- 5 In a 1,000-ml three-neck flask, there were mixed 200 grams of aluminium trisethylglycolate (Al content 6.8 wt.%) and 38.6 grams of ethyl glycol with 38.6 grams of silicon tetraethanolate (28.5 wt.%). This mixture was added in three portions to 360 g of water heated to 30 °C in order to perform the hydrolysis. Hydrolysis took 1.5 hours. Then, 4.4 grams of 25 % ammonia solution were added. After phase separation, the supernatant organic phase was decanted. The alcohol in the aqueous phase was eliminated by steam distillation, followed by spray drying.
- 10

Example 7 (Comparative Example Compound C)

- 15 Into a 2,000-ml three-neck flask, there were placed 638 grams of aqueous silicic acid. The contents was heated to 75 °C. A total of 500 grams of aluminium trishexanolate (Al content 6.35 wt.%) were added in three portions at time intervals of 15 minutes. After stirring for 30 minutes, the alcohol was decanted and the residue was diluted to a solids content of 5 %. The sol was heated to 95 °C and maintained at this temperature for 5 hours. The remaining aqueous phase was liberated from alcohol residue by steam distillation, followed by spray drying.
- 20

25

30

35

10054830-012302